II.H H_2 Delivery

II.H.1 Hydride Based Hydrogen Compression

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Objectives

- Develop a hydride thermal hydrogen compressor that operates in conjunction with advanced hydrogen production technologies and improves the efficiency and economics of the compression process.
- Construct and test a single stage thermal compressor that employs miniature hydride heat exchangers and three purification technologies to determine threshold contamination levels (levels at which compressor performance is affected) for H_2O, O_2, CO, CO_2 and CH_4.
- Investigate compressor capabilities to perform the dual function of compression and removal of impurities that adversely affect fuel cell operation (CO and CH_4).
- Engineer and test hydride alloys suitable for long term operation at pressures over 5,000 psig.
- Validate the entire compressor process in a multi-stage, pilot scale system.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- Hydrogen Delivery
  - B. High Costs of Hydrogen Compression
- Hydrogen Storage
  - S. Cost
  - T. Efficiency

Approach

- Assess feasibility
  - Quantify H_2 quality anticipated from renewable production techniques.
  - Preliminary design and safety analysis.
- Validate and test
  - Determine hydride alloys' resistance to disproportionation[1].
  - Validate compressor operation to >5,000 psi.
  - Determine hydride alloys' tolerance to impurities while cycling.
  - Test effectiveness of three purification techniques (passive purification for H_2O & O_2, elevated temperature desorption for CO & CO_2, inert gas venting for N_2 & CH_4).

- Refine process design
  – Determine if compression with purification is a viable alternative for improving fuel cell performance.
  – Reduce capital cost via miniature hydride heat exchangers and rapid cycling.

Accomplishments

- Determined that hydride compression's low energy cost will substantially reduce the cost of high pressure hydrogen.
- Demonstrated thermal compression to 8,000 psia with a clear path to 10,000 psia.
- Reduced hydrogen CO content from 1,000 ppm to less than 5 ppm to protect fuel cell catalyst.
- Removed inert gas species using a novel venting technique.
- Refined process design to reduce size and cost via miniature hydride heat exchangers with extended surface tubing to approach the 2010 cost targets of $0.14 to $0.16/kg (3,000 to 6,000 psi).

Future Directions

- Full-scale hydride thermal compression demonstration with funding from private sources.

Introduction

The hydride compressor is an absorption-based system that uses the properties of reversible metal hydride alloys to silently and cleanly compress hydrogen; hydrogen is absorbed into an alloy bed at ambient temperature and, subsequently, is released at elevated pressure when the bed is heated. Compression energy can be supplied by hot water and, for the very high pressures being considered for on-board hydrogen storage, at a fraction of the energy cost of mechanical compression. The primary technical objective of this project is to determine whether hydride compressors can be used for non-pure hydrogen streams likely to result from advanced hydrogen production methods (i.e. from renewable resources), with the commercial objective of developing a viable hydride compressor that offers substantial benefits over mechanical compressors.

A pilot scale hydride thermal compressor was built and is being tested to determine the extent to which a hydride compressor can both tolerate and remove impurities from the hydrogen stream. In particular, CO is present in hydrogen from many advanced production processes and must be removed to prevent damage to the fuel cell electrode catalyst. Removing CO in the compression process can be more cost effective than other hydrogen purification schemes. A process has been developed that reduces carbon monoxide levels to less than 5 ppm. In addition, the compressor employs miniature hydride heat exchangers to reduce capital cost and has operated to pressures in excess of 8,000 psia.

Approach

Hydride-based hydrogen compression is a comprehensive project with three phases: feasibility, validation and test, and product refinement. A full scale demonstration at a hydrogen production facility is anticipated following the completion of the current project.

In the feasibility phase of the project, we investigated the application of thermal hydrogen compression to hydrogen produced from renewable resources and developed a preliminary thermal compressor design for comparison with conventional mechanical compressors. A hazardous operation safety analysis of the thermal compressor system was completed. Thermal hydrogen compression was found to have distinct operational and economic advantages over mechanical compression for a majority of advanced hydrogen production processes. [1]

In the validation and test phase of the project, a pilot-scale compressor and test stand were built and are being operated to determine the extent to which a hydride compressor can both tolerate and remove impurities from the hydrogen stream. The compressor includes three purification techniques: passive purification for H_2O & O_2, elevated temperature desorption for CO & CO_2, and inert gas venting for N_2 & CH_4. Testing is nearing completion and excellent results have been achieved and are reported below.

Process refinement has been a continuous process over the course of the project. Refinement in previous years included reducing complexity and cost of the compression process through the identification of disproportionation resistant hydride alloys which allow operation at higher temperatures [2] [3], the demonstration of hydride compression to 8,000 psia with a clear path to 10,000 psia [4], and competitive analysis of mechanical and hydride compression to 5,000 psia indicating that hydride compression energy cost is 60% less than mechanical compression. [4] This year, manufacturing techniques were developed for miniature, modular hydride heat exchangers to reduce capital cost.

Results

CO Elimination

HERA developed and demonstrated a novel CO elimination process, elevated temperature desorption, that allows the hydride compressor to tolerate and remove CO from the hydrogen stream. Last year we reported results with hydrogen feed containing 300 ppm CO [4] and this year we increased the CO inlet content to 1,000 ppm.

The composition of the compressor discharge with the CO elimination feature is depicted in Figure 1. The CO elimination process results in a reduction of CO from 1,000 ppm at the compressor inlet to less than 5 ppm, in order to protect the fuel cell catalyst. Figure 1 illustrates that most of the CO is converted into methane (CH_4) and the methane is released in large spikes (>5,000 ppm) at the beginning of each desorption cycle. This suggests that methane could be removed from the hydrogen stream via inert gas venting, using an economically small amount of hydrogen.

CH_4 Removal Using Inert Gas Venting

The term "inert gas" as used in this paper refers to gas species that do not react with hydride alloys at

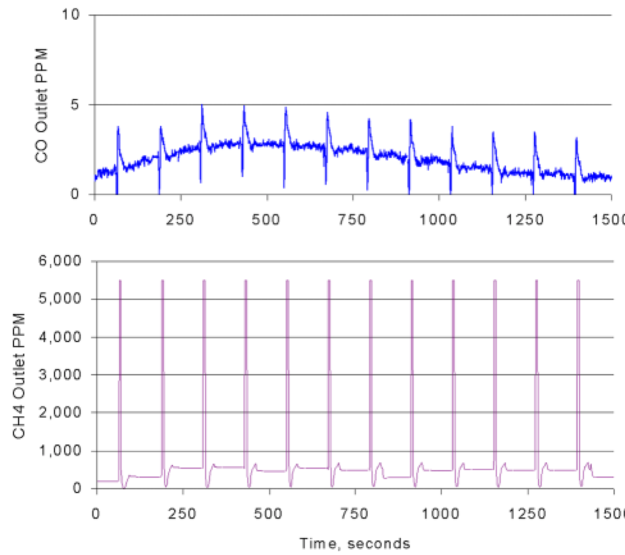

Figure 1. The CO Elimination Feature Reduces Outlet CO Concentration from 1,000 ppm to Less Than 5 ppm

the compressor's modest operating temperatures. "Inert gas" includes noble gases, such as helium and argon, as well as nitrogen and methane.

During a hydrogen absorption cycle, inert gas impurities flow with the hydrogen into the hydride bed, but are not absorbed by the hydride alloy. They tend to concentrate on the surface of the alloy particles within the alloy bed. In order to remove these impurities from the hydrogen stream, the hydride compressor includes a fast acting, solenoid vent valve. Hydrogen released during a momentary opening of the vent valve should sweep away inert gas species from the hydride bed. The vented gas will be routed to the hot water heater to recapture its heating value.

Initial tests to remove methane using the vent valve proved less than satisfactory. Figure 2 depicts the outlet hydrogen methane content after venting, including a brief period during which methane concentration exceeded 5,400 ppm, the upper detection limit of the methane analyzer. Integrating the area under the curve shows that very little methane was removed during the venting process. It was determined that the water adsorbent used to maintain fast reaction kinetics in the passive purification process [5] also dynamically adsorbed methane, preventing its removal during inert gas venting.

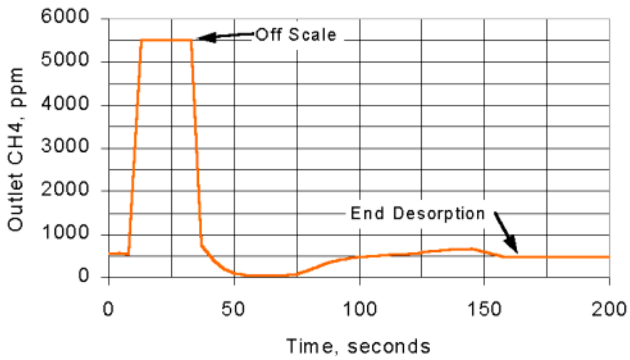

Figure 2. Initial Results with Inert Gas Venting Indicated CH_4 was Difficult to Eliminate

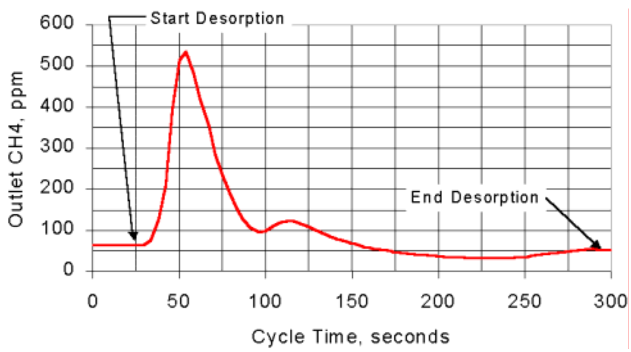

Figure 3. Modifying Operating Conditions Allowed the Removal of More Than 90% of the CH_4

The compressor operating conditions were modified to improve the inert gas venting process, resulting in a dramatic decrease in outlet methane content, as shown in Figure 3. Methane removal efficiencies over repeated cycles ranged from 90 to 92%. The alloy previously engineered for the first compressor stage (where inert gas venting occurs) was not ideally suited for the modified operating conditions. This resulted in an increase in the amount of hydrogen released during venting to an unacceptable level of 19 to 24%; however, knowledge gained about the interactions among the three purification processes indicate that the amount of hydrogen required for venting can be reduced to a level of less than 3.5% when compressing hydrogen with 1,000 ppm CO.

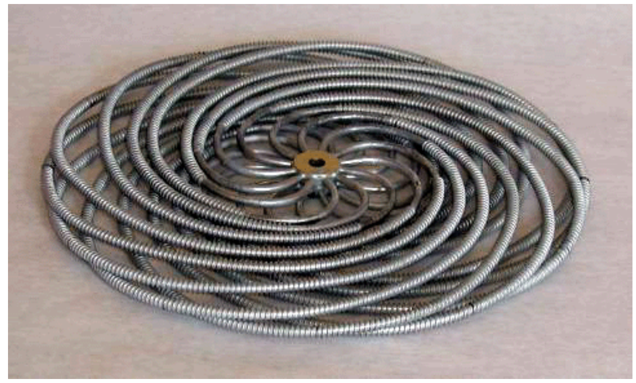

Figure 4. HERA's Ring Manifold Hydride Heat Exchanger Can Be Mass Produced to Reduce Costs

Reducing Capital Cost Using Miniature, Modular Hydride Heat Exchangers

Capital cost reduction efforts were focused in three areas: developing an inexpensive method to double heat transfer surface area, increasing kinetics to reduce heat exchanger size and cost, and demonstrating a cost effective method to simultaneously bond multiple tube joints that can be leak tested before final assembly of hydride heat exchangers. Figures 4 and 5 show full scale ring manifold heat exchangers that were constructed of finned tubes.

The finned-tube ring manifold substantially reduces compression cost per kg of hydrogen produced in a refueling station-sized compressor. While compression costs using bare, straight tube, welded heat exchangers are currently estimated at \$0.45 to \$0.48/kg in quantities of 100, we estimate hydride compressors using finned-tube ring manifolds should be able to approach the 3x cost reduction required to meet the 2010 targets of \$0.14 to \$0.16/kg (3,000 to 6,000 psi).

Conclusions

- The hydride hydrogen compressor prototype demonstrated high compression, tolerance to impurities, and the ability to both compress and purify hydrogen.

Figure 5. Modular Heat Exchangers Enable Meeting DOE Compression Cost Targets

- Of particular importance to protecting the fuel cell catalyst, CO impurities were reduced to less than 5 ppm.
- Miniature modular hydride heat exchangers enable capital cost reduction aimed at meeting the year 2010 compression cost targets.
- An energy cost analysis shows hydride compression substantially reduces the delivered price of high pressure hydrogen.
- Knowledge of impurity-effects on compressor hydrides establishes a baseline for understanding impurity impact on advanced storage materials (alanates, complex hydrides & carbon nanomaterials).

HERA USA Inc. is actively marketing commercial compressor systems that incorporate designs developed within this project.

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